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| <p>(54) Title: PECTIN-CONTAINING PRODUCT AND METHOD FOR PRODUCING SAME</p> <p>(57) Abstract</p> <p>A novel low-cost crude pectin-containing vegetable product prepared from agricultural waste products and a method for the production thereof. The product comprises 5-45 % pectic substances of which at least 25 % are in a water-soluble form. The pectic substances of the product has a degree of esterification in the range of 45-90 %. The product is useful as a thickening and gelling agent, as a water absorbing agent and as a dietary fibre additive, especially for lowering the cholesterol levels in the blood.</p> | | |

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PECTIN-CONTAINING PRODUCT AND METHOD FOR PRODUCING SAME

FIELD OF INVENTION

The present invention provides a novel low-cost crude pectin-containing vegetable product prepared from agricultural waste products and a method for the production thereof. The product comprises 5-45% pectic substances of which at least 10% are in a water-soluble form. The pectic substances of the product has a degree of esterification in the range of 45-90%. The product is useful as thickening and gelling agents, as a water absorbing and/or water holding agent and as a dietary fibre additive especially for lowering the cholesterol levels in the blood. The method of production which is provided comprises a treatment of the starting material with an acid, an acid-producing microorganism or a suitable enzyme to obtain conversion of at least part of the water-insoluble pectic substances to water-soluble pectin, under conditions where water is added in an amount which will result in a water content not substantially higher than the original water content of the starting vegetable material in its fresh state.

TECHNICAL BACKGROUND AND DESCRIPTION OF THE PRIOR ART

The term "pectic substances" is used to cover a group of colloidal heteropolysaccharides found in plants and composed predominantly of polygalacturonic acids formed by the chainlike combination of anhydrogalacturonic acid residues. Some of the carboxyl groups of the polygalacturonic acids are esterified with methanol and some are usually neutralized by one or more alkaline substances. When occurring in plant tissues, pectic substances are in a water-insoluble form for which the general term protopectin is used. When subjected to restricted hydrolysis, protopectin yields pectinic acids which are polygalacturonic acids of colloidal nature in which some of the carboxyl groups are

esterified with methyl groups. The term pectin designates pectinic acids which contain at least about 3% methyl ester groups, expressed as methoxyl, and which are capable of forming gels with in the presence of sugar and acid under
5 suitable conditions.

Besides galacturonic acid residues, pectic substances contain L-rhamnose residues which are bound to the main chains of polygalacturonic acids. These L-rhamnose residues act as sites for a more random branching comprising other
10 sugars such as D-glucose, D-galactose, L-arabinose, D-xylose, D-mannose, and L-fucose whose occurrence vary from one pectin source to another. Branching is also known to occur at sites of some of the galacturonic acid residues. As a result of this branching, pectin can build up a hydrophilic three-dimensional network with a considerable water
15 holding capacity. In general, pectin comprises 60-70% galacturonic acid.

Pectin occurs in all higher land plants, especially vascular plants in all parts of the plants e.g. in roots, stems, leaves, and particularly in fruits such as apples, lemons and lime where it is located in the primary cell
20 walls and in the middle lamellas in the form of water-insoluble protopectin, together with cellulose and pentosans. The molecular weight of water-soluble pectin resulting from hydrolysis of protopectin varies considerably but
25 is typically less than 200000.

The exact nature of pectic substances as they occur in plants is not completely understood. There is, however, a very complex molecular arrangement between protopectin and
30 the other cell wall components involving covalent and hydrogen bonds. Furthermore, metal ions such as Ca^{++} and Mg^{++} are also involved by complex binding to the pectic substance.

The main sources of commercial pectin products are citrus peel and apple pomace in which protopectin represents 10-40% of the dry weight. Pectin is mostly obtained from the plant material by treating the material with an acid or a base under suitable conditions, whereby the protopectin is split, followed by extraction of the water-soluble pectin. In industrial production of pectin acid or base treated plant starting material is subjected to a subsequent extraction with dilute acid, which step is followed by separating the depectinated plant material by e.g. filtration or centrifugation to obtain a viscous extract containing up till 1% soluble pectin. This extract may be purified and processed further. Finally, the pectin is precipitated, separated and dried to obtain the commercial pectin product.

Depending on the processing conditions (pH, temperature and time of extraction), it is possible to control the process so that pectins having different degrees of esterification are obtained. The hydrolysis of the galacturonic acid methyl esters occurs at both acidic and alkaline pH values, but dominates at pH values above 7 where this reaction is accompanied by depolymerization through β -elimination.

Pectin is commonly known for its gelling properties, the degree of which depends on the proportion of galacturonic acid residues which are in methyl ester form. Commercial pectin products used as gelling agents fall into two groups: (1) High-methoxylated pectins with a degree of esterification higher than 45% and (2) low-methoxylated pectins having a degree of esterification less than 45%. Pectin is of significant importance in the food industry as a gelling and stabilizing agent in the manufacturing of food products such as jams, jellies, preserves, milk products, cheese products, snacks and ice cream. Furthermore, the gelling characteristics of pectin is utilized in other technical fields e.g. in the manufacturing of pet food,

cosmetics, pharmaceuticals, paper, textiles and paints, and in the drilling industry.

Together with other plant components including cellulose, hemicellulose and beta-glucans, pectic substances are
5 classified as dietary fibres which also includes other complex polysaccharides of natural origin, e.g. alginates, carrageenan and agar from marine plants, gums and mucilages such as guar, psyllium seed gum and locust bean gum. Several disorders, especially cardiovascular and gastrointes-
10 tinal disorders prevailing in the human population in industrialized countries have been associated with shortages of dietary fibres in the daily diet. Both human and animal studies have indicated that dietary fibres have beneficial physiological effects such as a depression of
15 blood serum cholesterol, improved blood glucose management in diabetic patients, lowering of blood pressure in hypertension, lowering of the risk of developing colon cancer, and aiding in control of body weight in overweight persons. Since dietary fibres comprise a rather diversified group of
20 compounds it is not surprising that it has been found that the physiological effects thereof to some degree depend on the type of fibres and physical and chemical characteristics of the particular type of fibres.

Amongst the beneficial physiological effects which have
25 been associated with pectin, the ability hereof to reduce serum cholesterol levels (the hypocholesterolemic effect) in humans and in animals has during recent years attracted particular attention. Reported results from laboratory studies and human clinical trials are supportive evidence
30 of this physiological effect. Based on results of feeding trials with rats it has also been demonstrated that highly esterified pectins are more effective in reducing cholesterol levels than low-esterified pectins.

Major sources of raw materials for the production of pec-
35 tin-containing products are vegetable waste products from

juice processors, sugar beet refineries and other plant material processing industries. As it has been described hereinbefore, pectin may be obtained in a substantially pure form by precipitating acid or alkaline extracts of vegetable materials, separating the precipitate which is optionally purified and subsequently dried. A process for obtaining pectin products in substantially pure form, however, involves considerable costs which seriously restricts the areas of application for such products. Therefore there have been several attempts to develop useful crude pectin-containing products and production methods therefor.

Such a product, useful for thickening of rubber lattices is described in US 2.132.065 which discloses a crude pectated product obtained by treating citrus pulp with sodium carbonate at a pH between 7 and 8.5 at a temperature not exceeding 35°C. Following this treatment any free liquid is drained off and the resulting product is washed with water and allowed to drain, dewatered by pressing or centrifugation and dried. The resulting product has a low degree of esterification. GB 1.508.993 deals with a food product comprising a solid foodstuff and an aqueous phase which is thickened or gelled by a pectic substance with a degree of esterification less than 20% which substance is prepared by subjecting a natural pectin source, e.g. citrus peel to alkaline deesterification at a pH between 7 and 8 by treatment with an alkaline compound such as sodium carbonate.

A citrus fibre additive for grain flour is described in US 4.225.628 which discloses a product obtained from citrus waste by neutralizing the natural acid content thereof by adding calcium hydroxide or oxide to obtain a pH of 5.5 to 7.0 and then pressing out water and soluble components. The pressed material may be dried and used as is or it may be blended with a high protein flour prior to drying. Another pectin-containing food additive which is useful as a texture improving agent for various food products is disclosed

in JP 56015654. This additive is prepared from the skin of citrus fruit which after extraction with an organic solvent to remove oily substances is reacted with alkaline calcium and/or magnesium compounds thereby partly converting the
5 pectic substances to calcium and/or magnesium salts.

GB 2.145.103 discloses a highly water-absorbing pectin-containing product comprising from 15% to 60% pectin having a degree of esterification ranging from 1% to 45% and less than 50% of the pectin being in the form of a divalent
10 metal salt. Suitable raw materials are citrus pulp and sugar beet pulp. The product is prepared by comminuting the vegetable material, deesterifying the pectin contained therein to a degree of esterification of less than 45%, followed by a dewatering step, washing with water and
15 finally drying the resulting material to obtain the product. The step of deesterification may be carried out at acid or alkaline pH, but it is preferred to use an alkaline treatment since acid deesterification is too slow and results in an undesirable extraction of divalent cations and
20 degradation of hemicellulose. The preferred alkaline deesterification is carried out within a pH range of 9-12 at a temperature of 25°C or lower. It is stated that a degree of esterification of less than 45% is important to obtain satisfactory wicking properties of the absorbent material
25 which properties are considered to be determinative for the water holding capacity.

US 4.497.838 discloses a product obtained by extraction of citrus peel with a non-aqueous water miscible solvent whereby sugars, essential oils and bioflavenoids are removed from the peel. After drying and comminuting the solvent-extracted peel, a product is obtained which is rich in cellulose and pectic substances and having a high water holding capacity. The product is useful as a thickening, emulsifying or stabilizing agent and as a hypocholesterolemic agent. JP 63216822 discloses a cholesterol-lowering fibre composition prepared from sugar beets by removing

soluble components by extraction with warm water.

JP 57054573 describes a dietary fibre product prepared by treating pressed sugar beet pulp with a weak hypochlorous acid solution at pH 6.5 to 7.5 followed by washing and
5 drying. Other dietary fibre products have been made by treating vegetable materials rich in fibres with solutions of bleaching agents such as hydrogen peroxide. Such products are disclosed in e.g. US 4.241.093 and US 4.806.475.

The degree of esterification of water-soluble pectic substances determines the physical and physiological characteristics of these useful compounds. The majority of the commercial, substantially purified pectin products which are predominantly applied as gelling agents in the food industry have a degree of esterification of 45% or more. In
10 order to preserve this desired high degree of esterification in substantially pure pectin products the extraction of pectin is usually carried out under acidic conditions, since alkaline treatment enhances deesterification. However, it is not known in the prior art to produce low-cost
15 crude pectin-containing products having a high degree of esterification by treating vegetable waste materials with acid to convert a desired amount of protopectin to water-soluble pectin under conditions which results in a product having at the same time excellent gelling characteristics,
20 a significant cholesterol-lowering effect and a high water holding capacity.
25

SUMMARY OF THE INVENTION

The present invention relates to a crude pectin product containing plant tissue material with microscopically
30 recognizable plant tissue structures having a dry matter content of at least 85% wherein the dry matter comprises 5-45% by weight of pectic substances having a degree of esterification of more than 45% of which pectic substances more than 10% is in a water-soluble form. The dry matter

further comprises 5-15% by weight of ashes comprising a proportion of alkaline and/or alkaline earth metals in the range of 30-50% by weight, and 40-90% by weight of non-pectic plant cell material comprising cellulose, hemicel-
5 lulose, organic acids and water-soluble carbohydrates. The product is further characterized in that the pH of a 1% aqueous suspension thereof is in the range of 3-5, the reduced viscosity of its water-soluble pectic substances is in the range of 0.050 to 0.500 L/g, and in that the water
10 holding capacity is at least 4 g water/g, and in that it has a reducing effect on the levels of cholesterol in blood serum and liver of animals when fed thereto.

In a preferred embodiment of the invention there is provided a product which is in the form of a substantially free-
15 flowing powder consisting essentially of particles of a size of at the most 1.0 mm.

In another aspect, the present invention relates to a method for producing a product as defined above, which method comprises subjecting plant tissue material contain-
20 ing pectic substances and having microscopically recognizable plant tissue structures to conditions which will convert at least part of the water-insoluble pectic substances to water-soluble pectic substances in which substances the degree of esterification initially present in
25 the water-insoluble pectic substances is substantially preserved, followed by drying the resulting material to obtain the product with a water content of 15% by weight or less and optionally comminuting the dried material, substantially without at any stage adding water in an amount
30 which may result in a water content higher than the original water content of the plant tissue material in its fresh state, the drying of the material being performed without any substantially concomitant removal of dry matter, such as by evaporation of water. It is preferred that the plant
35 tissue material has a high content of pectic substances,

and materials which on a dry matter basis contains more than 15% by weight of pectin are particularly useful.

In a preferred embodiment, the method comprises the addition of an inorganic or an organic acid to the plant tissue starting material in an amount sufficient to reduce the pH to 1-3, keeping the resulting mixture at a temperature and for a period of time sufficient to obtain the desired conversion of insoluble pectic substances to the water-soluble form, followed by adjusting the pH to a higher pH within the range of 3-5 by the addition of a base.

The crude pectin product is useful for a number of applications including water absorption and/or water holding, gelling of aqueous suspensions, and as a dietary adjunct e.g. as a cholesterol-reducing agent. In a further aspect, the invention therefore relates to the use of the product as a water absorbing and/or water holding agent, as a gelling agent and as a dietary fibre additive.

DETAILED DESCRIPTION OF THE INVENTION

One object of the present invention is to provide a novel inexpensive crude pectin-containing product having a dry matter content of at least 85%. In the context of the invention the term "crude" is used to describe a pectin-containing product which comprises at least all water-insoluble components of the vegetable pectin-containing starting material in which material plant tissue structures are microscopically recognizable, these components optionally being present in the product in a modified form relative to the starting material.

It is essential that the dry matter (DM) content of the product is at least 85%. At lower DM contents the storage stability of the product will be reduced to an unacceptable level since at such lower DM contents the product will be

prone to deterioration by chemical and microbiological processes. In order to restrict such deterioration processes to the a commercially preferable level it is considered advantageous to increase the DM content to at least 90%,
5 and in particular to a 95%. However, products having such low water contents may absorb humidity from the surrounding atmosphere. It may therefore be necessary to provide the product of the invention in a packaging consisting of materials which are water vapour tight, e.g. plastic foils
10 or metal foils. Alternatively, the low water content may be maintained by the incorporation of suitable water absorbing compounds such as silica gel.

On a dry matter basis the product according to the invention comprises 5-45% pectic substances calculated as galacturonic acid.
15

In this context the term "pectic substances" is used to describe the total content of polygalacturonic acid-containing components in the product and it includes both water-insoluble protopectin and water-soluble pectic substances.
20 Protopectin is a term which is used to describe pectic substances as they occur naturally in plant materials. These native pectic substances are insoluble in cold water but will give rise to water-soluble pectic substances upon a variety of treatments such as heating with water,
25 treatment with acids, or ion-exchange agents. One reason why protopectin is insoluble in water is that protopectin is a pectin-cellulose complex.

The method for determining the content of galacturonic acid is described hereinbelow. The proportion of galacturonic
30 acid in pectic substances varies according to the vegetable source and to the physiological stage of the particular plant from which the substances are derived. According to the present invention the water-soluble pectic substances in the product have a galacturonic acid content of at least

50%. It is contemplated that the present water-insoluble protopectin has a similar content of galacturonic acid.

The dry matter of the product according to the invention comprises 5-45% by weight of pectic substances as defined
5 above. It is, however, preferred that the total proportion of pectic substances in the dry matter is at least 25% by weight. The final content of pectic substances in the product depends on the amount hereof present in the starting plant tissue material. The invention is based on the
10 findings that a treatment of plant tissue materials in which essentially all pectic substances occur as protopectin with acid during which a restricted amount of water is added so that the total amount of water at any stage of the treatment does not substantially exceed the water content
15 of the plant tissue materials in their fresh state, results in a conversion of 10-80% of the water-insoluble protopectin to water-soluble pectic substances. It is preferred that the proportion of pectic substances in the product which is converted to the water-soluble form is at least
20 30% by weight, preferably at least 50% by weight, and in particular at least 50% by weight.

The calculation of the proportion of water-soluble pectin in the products according to the invention relative to the total content of pectic substances is explained in details
25 in Example 2 hereinbelow.

It is believed that the usefulness of the pectin-containing product is predominantly attributable to the content of pectic substances and to the physical and chemical characteristics thereof. As explained hereinbefore pectic sub-
30 stances are predominantly composed of linear chains of D-galacturonic acid residues. In the natural state most of the carboxyl groups of these acid residues are esterified with methanol. It has long been known that the degree of esterification (DE) of pectins is a major factor in deter-
35 mining the technological characteristics of these products

and it is common to classify pectins according to their ester content.

It is known that the DE has an effect on the water absorption characteristics of dried pectic substances, e.g. when they are used as water absorbing and/or water holding materials in disposable diapers, sanitary napkins and similar products. It is generally believed that in order to be suitable as an absorbent material in the above products pectic substances must have a DE of less than 45%, preferably less than 20%. It has now been found that a crude pectin product can be produced which has a high water holding capacity even if the DE is in the range of 45-90%. Furthermore, a relatively high DE is preferred when pectic substances are used as dietary fibre preparations especially when they are used with the aims of reducing the cholesterol levels. It is believed that this beneficial effect is particularly associated with highly methoxylated pectins.

A particularly interesting aspect of the present invention is therefore to provide a crude pectin product comprising a large proportion of highly methoxylated pectic substances. The product contains pectic substances wherein the degree of esterification is in the range of 45-90%. In a preferred embodiment, the degree of esterification is at least 60%

The water-soluble pectic substances according to the invention are characterized in that they have a galacturonic acid content of at least 50% and a content of acid and alcohol insoluble solids (AAIS) in the range of 60-90% by weight as defined as solids remaining after washing with acidic 60% isopropanol. These insoluble solids comprise pectin, cellulose, and proteins. By the washing procedure soluble carbohydrates, salts and water are removed. AAIS is determined essentially according to the method described in Food Chemical Codex, 2nd edition, 1972, p. 580. Furthermore, the water-soluble pectic substances of the powder has a reduced viscosity (η_{red}) which is at least 0.050 L/g and

preferably in the range of 0.250 to 0.500 L/g. The term "reduced viscosity" in the present context is used as an indirect indication of the mean molecular weight. Initially the specific viscosity of a pectin solution in 1% hexameta-
5 phosphate, pH 4.5 is determined by measuring dropping periods of the pectin solution and the buffer solution at 20°C in a falling ball viscometer (Hoeppler).

The specific viscosity, η_{sp} is defined as: (dropping period for pectin solution/dropping period for buffer
10 solution) - 1. The reduced viscosity is defined as η_{sp}/c (L/g) where c is the concentration of pectin.

The product has a pH in the range of 3-5, preferably in the range of 3.5-4.5 when a 1% aqueous suspension is measured. Within this pH range the stability of the pectin is high.

15 The crude pectin-containing product has a water holding capacity (WHC) of at least 4 g water/g. In the present context, the water holding capacity is defined as the amount of water which is retained per g of product when 0.5 to 1 g of product having a particle size of at the most 1.0
20 mm is soaked in 10 ml demineralized water at ambient temperature for 30 minutes, followed by centrifugation of the soaking mixture for 10 minutes at 240 x g and measuring the amount of water retained. The water holding capacity of the product depend i.a. on the particle size, the content of
25 pectic substances, the chemical composition thereof and on the raw material source. Preferably, the water holding capacity is at least 9 g water/g. The product produced according to the method of the invention from lemon or lime fruit peels has a WHC of 9.6-9.7. In comparison to cor-
30 responding values for the dried raw materials this is an increase of about 60-90%. The high WHC of the powder makes the product useful as a water absorbing material in e. g. disposable diapers and sanitary napkins. It is furthermore believed that a dietary fibre product is particularly

suitable for reducing cholesterol levels when the WHC is high.

In a further aspect of the invention there is provided a pectin-containing product which when fed to rats in cholesterol reducing amounts for at least a period of 3 weeks results in a reduced amount of serum and liver cholesterol of the animals relative to amounts of serum and liver cholesterol of control animals fed a diet not containing the product. The feeding trial is described in details in the below Example 9. As it appears from the result of this trial, both blood serum and liver cholesterol levels were reduced by more than 25% and the concentration of serum triglycerides was reduced as well. It is known from a large number of human and animal studies that water-soluble pectic substances in addition to other dietary fibre compounds reduce the level of blood serum cholesterol. The mechanisms by which dietary fibres including pectin exerts their hypocholesterolemic effects are not elucidated. It has been indicated that the capacity of the fibre products to exert the effect is related to their ability to bind certain bile salts such as deoxycholates. It has been found that this binding is enhanced in the presence of calcium ions. It is therefore contemplated that it is advantageous that the present product comprises a high amount of calcium ions.

The dry matter of the product according to the invention comprises 5-15% by weight of ashes. The term "ashes" in this context designates the non-combustible residue comprising inorganic compounds which are left after combustion of the present product by placing a sample hereof overnight in a furnace preheated to 600°C. The resulting ashes comprise predominantly alkaline metal ions, alkaline earth metal ions and one or more inorganic acid residues such as sulphate, phosphate, nitrate or chloride. Preferably the ash content is at least 8% by weight. The total content of ashes depends on the composition of the vegetable raw

materials and on the amounts of acid and base added during the production of the product.

Furthermore, the dry matter of the product according to the invention comprise 40-90% by weight of non-pectic plant tissue material. The composition of this material will vary considerably depending on the source of pectin-containing plant raw material. Provided the raw material has not been subjected to a washing step prior to being used in the preparation of the crude pectin product the non-pectic plant material will comprise all non-pectic substances of the particular plant raw material such as cellulose, hemicellulose, starch, water-soluble carbohydrates, proteins, and organic acids. When an initial washing of the plant raw material is carried out at least part of the water-soluble substances of the plant material will be removed including water-soluble carbohydrates and organic acids.

The crude pectin product as defined above may be in any suitable and convenient particle size and form. In one preferred embodiment the product is in the form of a substantially free-flowing powder consisting essentially of particles of a size of at the most 1.0 mm.

In a particular aspect of the present invention there is provided a method for producing a product as defined above, which method comprises subjecting plant tissue material containing pectin substances and having microscopically recognizable plant tissue structures to conditions which will convert at least part of the water-insoluble pectic substances to water-soluble pectic substances in which substances the degree of esterification initially present in the water-insoluble pectic substances is substantially preserved, followed by drying the resulting material to a water content of 15% by weight or less and optionally comminuting the dried material to obtain the product as defined hereinbefore, without at any stage adding water in an amount which will result in a water content substantial-

ly higher than the original water content of the plant tissue material in its fresh state, said original water content being at the most 90% of the plant material fresh weight, the drying of the material being performed without
5 any substantial concomitant removal of dry matter, such as by evaporation of water.

Plant tissue materials which are suitable as raw materials in the practice of the invention comprise any plant material which has a high content of pectic substances and which
10 is readily accessible at a competitive price. Suitable raw materials are plant tissue materials which in their dry matter contain at least 5% by weight, preferably at least 10% by weight, and in particular at least 15% by weight of pectic substances.

15 Such suitable raw materials include peel, pulp and/or rag from citrus fruits such as lemons, oranges, mandarins, limes, grapefruits, tangerines and shaddocks, apple and pear pomace, potato peel, sugar beet pulp, skin of grapes, pea pods, and carrot fibre materials. Whole fruits and
20 vegetables such as tomatoes, quinces, mangoes, pineapples, onions, olives, wood apples, bread fruits, plums, strawberries may also be utilized as sources of raw material.

Especially preferred sources of raw materials for the product according to the present invention are citrus fruit
25 peel, apple pomace and sugar beet pulp. These raw materials all have a high content of pectic substances in the form of water-insoluble protopectin. Citrus peel in which the content of protopectin is in the range of 30-35% on a dry matter basis is particularly preferred. Apple pomace and
30 sugar beet pulp dry matters have a content of water-insoluble pectic substances in the range of 15-20%. Other pectic substance raw materials may be selected even if their content of protopectin is less than that of the preferred raw materials, e.g. if they are available at a

competitive cost. It may also be appropriate to use mixtures of two or more plant raw materials.

As it has been explained above, the degree of esterification of the pectic substances is an important factor which
5 determines the favorable properties of the resulting crude pectin product. The selected raw materials therefore comprise pectic substances in which the degree of esterification is in the range of 45-90%. Preferably, the degree of esterification is at least 60%.

10 The raw material may be used directly as it is obtained from the fruit or vegetable processing plants. However, it may be advantageous to carry out an initial washing with cold water to remove a substantial proportion of soluble carbohydrates, proteins, organic acids and salts. Optional-
15 ly, the plant raw material whether it has been subjected to an initial washing or not may be dried to bring down the water content to 15% or less. The drying may be carried out at temperatures ranging from ambient temperatures to about 150°C in any convenient drying equipment known per se such
20 as a drying oven, a fluid bed dryer or a band dryer. In the dried form, the plant tissue raw material can be stored for future use.

Preferably, raw material from overripe fruits in which enzymatic ripening processes have liberated water-soluble
25 pectin should be avoided since part of this pectin will be lost during an initial washing of the plant material. Furthermore, plant material in which more extensive enzymatic activity of pectin esterases has occurred is unsuitable as a raw material since the use hereof may result
30 in a final product comprising pectin with a reduced degree of esterification.

From a production cost point of view it may be advantageous to obtain a rapid conversion of the protopectin to the water-soluble pectin. It is contemplated that this may be

obtained i.a. by using raw materials having a large surface area relative to the mass, which can be brought into contact with those substances in the process mixture which give rise to the intended conversion of protopectin to water-soluble pectin. Prior to being processed, the plant tissue raw materials may therefore advantageously be divided into particles of a suitable size. In the present context a suitable particle size is meant to mean one which will ensure that the subsequent processing can proceed at the desired rate. Fresh material are conveniently comminuted in a blender or a fruit cutting machine, whereas dried raw materials may be milled, ground or crushed by means of any suitable equipment known in the art. Preferably, the raw materials are divided into a particle size being at the most 10 mm.

In a preferred embodiment of the invention whereby it is obtained that at least part of the water-insoluble pectic substances in the thus obtained divided plant raw material is converted to water-soluble pectic substances having the above defined characteristics, an inorganic or organic acid is added to the raw material in an amount sufficient to reduce the pH to a value in the range of 0-5, preferably in the range of 1-3, followed by keeping the resulting mixture at a temperature and for a period of time sufficient to obtain conversion of the desired proportion of non-soluble pectic substances to water-soluble substances.

When comminuted fresh raw material is used the acid may advantageously be added in a concentrated form in a volume of water which does not constitute more than about 5% of the total volume of the fresh plant raw material. Alternatively, dried finely divided plant material may be used as the starting material. In this case the concentrated acid is preferably added after dilution in a volume of water which is substantially equivalent to the amount of water which has been removed from the plant raw material during the initial drying process. The moisture contents of fresh

- plant materials are generally within the range of 70-90%. Provided the moisture content of dried raw materials used in the present invention is within the range of 5-15%, the proportion of acid-containing water to be added to the dried material is therefore preferably in the range of about 55 to about 85% relative to the resulting total volume of rehydrated plant material. The volume of concentrated acid used when dried plant materials are used depends on the pK-value of the acid and on the concentration thereof. Typically, the acid volume is in the range of 1-5% of the final volume. However, more dilute acid may be used in which case the volume of added water is reduced proportionately. Preferably, demineralized water is used to rehydrate dried plant material.
- Useful acids may be strong inorganic acids as exemplified by, but not limited to, hydrochloric acid, sulphuric acid, phosphoric acid or nitric acid. Also strong organic acids having pK-values of less than 3.5 may be useful. Examples of such suitable organic acids are formic acid, lactic acid, malic acid and oxalic acid.

As an alternative to the above direct addition of acid, the organic acid may be provided by the addition to the mixture of a culture of microorganisms which can convert at least some components in the plant tissue material such as water-soluble carbohydrates to organic acids as defined above. Examples of such useful microbial cultures are cultures of lactic acid bacteria which during fermentation produce significant amounts of lactic acid and smaller amounts of e.g. formic acid.

- Following the addition of acid and water to the plant raw material the resulting mixture is agitated, blended or kneaded while being kept at a temperature ranging from ambient temperature to about 100°C, a preferred temperature being from about 50°C to about 80°C. The reaction mixture is left to stand, optionally under constant agitation,

- blending or kneading at the selected temperature for a period of time ranging from 1 hour to 24 hours. Any suitable combination of temperature and time within the above indicated ranges which will lead to the desired conversion of protopectin to water-soluble pectin may be selected. The conversion period necessary under the selected temperature condition will to a large extent also depend on the acid concentration and the pK-value thereof. It may be possible to select reaction conditions which result in a protopectin conversion rate resulting in the desired conversion within a reaction period shorter than 1 hour. It may be advantageous that the physical affection during the holding period result in a further comminution of the plant material particles.
- 15 The conversion procedure as defined may be carried out as batchwise treatments, but it may be preferable to set up the procedure as a continuous process, wherein the plant raw material and the acid, optionally mixed with water is fed continuously to the reaction container concurrently with a continuous removal of plant material in which the desired conversion has been attained. The reaction conditions are selected so as to obtain the conversion of a desirable proportion of protopectin to water-soluble pectin substantially without any reduction of the initial degree of esterification. The desirable resulting proportion of water-soluble pectin is within the range of 10-80%, a preferred proportion being at least 40%, and a particularly preferred proportion being at least 50%.
- Notwithstanding the fact that the above described direct addition of acid to the protopectin-containing plant material is a preferred embodiment of the method according to the invention, it is anticipated that the desired conversion of protopectin may be obtained by alternative procedures including the addition of an enzyme with the ability of converting at least part of the water-insoluble pectic substances into water-soluble substances or the addition of

a microorganism which under the conditions prevailing in the plant raw material is capable of producing an enzyme as defined above. There have been described several enzymes acting upon pectic substances which are potentially useful in practice of the present invention. Protopectinase is an enzyme occurring naturally in fruits where it is responsible for the conversion of protopectin into water-soluble pectinic acids. Other enzymes capable of degrading pectic substances (pectolytic enzymes) include: pectinases such as pectin polygalacturonase and pectin depolymerases. Pectolytic enzymes are produced by several microorganisms belonging to bacteria, molds and yeasts, and some of these enzymes of microbial origin are commercially available.

When the required conversion into water-soluble pectin has been obtained the mixture is cooled to ambient temperature and pH is adjusted to a higher value within the range of 2.5-8, a preferred range being 3-5 by the addition of a base or a mixture of bases in an amount which is at least equivalent with the amount of added acid, whereby the resulting pH-value in the mixture is adjusted to the pre-treatment level or higher. The bases are selected from alkali metal compounds such as NaOH, KOH, K_2CO_3 , Na_2CO_3 , or $NaHCO_3$; alkaline earth metal compounds including $CaCO_3$, CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$, and $MgCO_3$; $Al(OH)_3$; or NH_4OH . Among the indicated compounds, magnesium and calcium compounds are particularly preferred. The alkaline compounds may be used as solid compounds or dissolved in water. Following the addition of base the mixture is stirred until the desired pH-value is achieved uniformly herein.

Subsequent to the adjustment of the pH by addition of an alkaline compound or a mixture of more alkaline compounds the resulting mixture is subjected to a drying procedure. The mixture may be dried as is or it may be advantageous to pre-treat the material by extrusion to pellets or other shapes. The drying step is carried out in a drying oven, a band dryer, a drum dryer or a fluid-bed dryer for a period

of time sufficient to reduce the moisture content of the material to at the most 15% by weight, preferably to at the most 10%, and in particular to at the most 5% by weight. The drying is carried out at a temperature ranging from
5 ambient temperature to about 150°C. It may be preferred to carry out the drying at air pressures below atmospheric pressures, whereby a relatively lower drying temperature or a comparatively shorter drying period can be used resulting in a more gentle treatment.

10 The resulting dried crude pectin-containing product is in the form of irregular particles, flakes, cakes or lumps, the form depending on the applied drying equipment. In a preferred embodiment this material is milled or ground by methods known per se in the art to a substantially free-
15 flowing powder having a particle size of at the most 1.0 mm.

The crude pectin product according to the invention is useful as a water absorbing and/or water holding material, a thickening and gelling agent and as a dietary fibre
20 additive. Presently, the application areas for pure pectin products is restricted due to the relatively high cost of these compounds. It is believed that the pectin component of the present crude product has essentially all of the technically valuable features of the pure pectin products
25 for which reason the product will have a very broad range of applications including most of those of the presently available commercial pure pectin products. As a water absorbing and/or water holding material it may be useful as a constituent of absorbent consumer products such as disposable
30 diapers and sanitary napkins. In the food industry the present product will be useful in essentially all product where pure pectin products are currently used, e.g. as a gelling agent in jams and jellies, confectioneries, bakery products or in frozen berries. In certain types of
35 bakery products such as hamburger buns the crude pectin product may counteract the tendency to development of

"toughness" of the product which is frequently observed when such products are frozen and thawed.

It has also been shown that the crude pectin product is useful in the manufacturing of beverages, especially beverage product which incorporates fruit tissue ingredients. In fruit juice products the addition of the crude pectin product can provide an increased viscosity resulting in a juice with an improved "mouthfeel" of richness when consumed. The present pectin product may also be useful as a thickening agent in cheese products and milk products such as sour milk products. Furthermore, the product may be useful as a stabilizer for frozen desserts or as a thickening agent in pet food products.

Pectin products are useful in the manufacturing of several types of pharmaceuticals. In spite of their broad applicability, however, relatively small amounts of pure pectin products find way into pharmaceutical use due to the high cost. It is therefore anticipated that the present low-cost pectin product may become more widely used in the pharmaceutical industry than the presently available products. Examples of potential applications are as a diarrhoea treatment product or as a demulcent in minimizing gastrointestinal irritation when irritating substances are administered. As a dietary fibre additive the product will be useful as a hypocholesterolemic agent as it has been explained hereinbefore. It is furthermore contemplated that the product will be useful for diabetic patients in their management of the blood glucose levels and for overweighed subjects as a dietary slimming product. As a pharmaceutical or a dietary adjunct the product may be used as is or it may be used as an ingredient in speciality food products.

The gelling or thickening properties of the product may be utilized in a number of technical uses. In particular, pectin functions well as an emulsion stabilizer for oil-in-water emulsions, e.g. in the paint industry. In the paper

and textile industry it may be useful as a sizing agent. Finally, it can be mentioned that the properties of the product make it potentially useful as an adjunct material in the drilling industry.

- 5 The invention is explained in further details in the following examples:

EXAMPLES

Materials and methods

Determination of dry matter

- 10 An accurately weighed sample is dried at 105°C for 2.5 hours in a heating cupboard and then transferred directly to a desiccator. When cooled the dried sample is weighed to obtain the dry matter content.

- 15 Determination of the content of acid and alcohol insoluble solids (AAIS).

- Three grams of sample, accurately weighed, are transferred into a beaker and stirred for 10 minutes with a mixture of 3 ml of concentrated HCl and 60 ml of 60% (v/v) isopropanol. The mixture is filtered through a dry, tared coarsely-sintered glass filter tube (30-60 ml capacity) and washed with six 9 ml portions of the acid/alcohol mixture, followed by 60% isopropanol, until the filtrate is free from chloride. Finally, the filter cake is washed with two 15 ml portions of isopropanol, dried at 105°C for 2.5 hours, cooled and weighed. This gives the acid and alcohol insoluble solids (AAIS).

Determination of the degree of esterification

An amount of AAIS determined as described above representing exactly 250 mg of the original unwashed sample is transferred into a 250 ml Erlenmeyer flask and moistened with 1 ml of ethanol. 100 ml of carbon dioxide free water is added. The mixture is stirred until the sample is completely dissolved. The solution is titrated with 0.1N NaOH to pH 9 using a pH meter with electrode. The volume required in ml is recorded as v_1 (initial titre). Ten ml of 0.5N NaOH is added and the solution is stirred vigorously for 15 minutes. Then 10 ml of 0.5N HCl is added and the solution is stirred until pH is stable. The solution is titrated with 0.1N NaOH to pH 9. The volume of 0.1N NaOH required in ml is recorded as v_2 (saponification titre). The degree of esterification is calculated according to the formula $100 \times v_2 / (v_1 + v_2)$.

Determination of the content of galacturonic acid

The weight in mg of galacturonic acid ($C_5H_9O_5COOH$) in the original unwashed sample is calculated according to the formula $(v_1 + v_2) \times 19.41$, in which v_1 and v_2 are the initial titre and the saponification titre, respectively, determined as described above.

Determination of the content of water-soluble pectin

100 g of sample material is suspended in 2000 ml of demineralized water at 70°C. After 1 hour the suspension is centrifuged and a weighed volume of the supernatant is diluted with 1.4 volume parts of isopropanol. The precipitated pectin is filtered off and dried. From the weight of the precipitated pectin the total amount of water-soluble pectin is calculated.

Determination of the reduced viscosity of pectin

A quantity of pectin corresponding to 90 mg pectin dry matter is weighed into a 150 ml Erlenmeyer flask together with 100 g buffer solution which is prepared by dissolving 1 g sodium hexametaphosphate in distilled water and adjusting the pH value to 4.5 with a few drops of 4N HCL. After a few hours of stirring the pectin is dissolved. If it is not clear the solution is filtered through a porosity 2-filter crucible. Dropping periods of the resulting pectin solution and the buffer solution, respectively are measured at 20°C in a "falling ball viscometer" (Hoeppler viscometer).

The specific viscosity is :

$$\eta_{sp} = \frac{\text{(Dropping period for pectin solution/dropping period for buffer solution)} - 1}{\text{concentration}}$$

The reduced viscosity is:

$$\eta_{red} = \eta_{sp}/c = \eta_{sp}/1 \text{ (L/g)}$$

Measurement of viscosity by means of a Haake Viscotester VT

2.4 g of the pectin product to be tested is weighed and placed in a 250 ml beaker (height 11.5 cm) by means of a glass spatula. The product is moistened with 5 ml of 96% (v/v) ethanol followed by the immediate addition of 100 ml of boiling water while stirring thoroughly with the spatula. The mixture is left to stand for 120 minutes at room temperature without agitation. However, if any tendency to lumping is observed during standing, the mixture is stirred with the spatula from time to time. After standing, distilled water is added to a total weight of 100.0 g and the viscosity of the resulting mixture measured by means of a Haake Viscotester, model VT 180 the thermostatic temperature control of which is adjusted to 25°C +/- 0.1°C.

The cup (NV) of the viscometer is filled to the mark with the reaction mixture and placed in the viscometer being switched on at speed 4, shear rate 252/second. Scale units are read after 180 seconds.

5 Determination of ash content

Three grams of sample is weighed accurately into a porcelain crucible and placed in a furnace preheated to 600°C and left to ash overnight. The crucible is then transferred to a desiccator, cooled and weighed.

10 Determination of Fe

One g of sample is ashed overnight at 550°C in a furnace. The crucible is cooled and a minimum volume of 2M HCl is added to dissolve the residue. The solution is transferred to a 25 ml volumetric flask and diluted with demineralized water to volume. A suitable aliquot of the solution is pipetted into a 50 ml volumetric flask. Ten ml of 2N nitric acid is added and the solution is heated for 2 minutes. The solution is cooled and 25 ml of isopropanol and 5 ml 1.3M ammonium rhodanide is added. The solution is diluted to the volume with demineralized water. The absorbance is measured at 500 nm (1 cm cell) using a PYE UNICAM SPI800 spectrophotometer. The Fe-content is obtained from a standard curve relating absorbance to known amounts of Fe in 50 ml solutions.

25 Determination of Na, K, Mg, Ca and SO₄

A 1 g sample is ashed as described above and dissolved in a minimum of 2M HCl, transferred to a 50 ml volumetric flask and diluted with demineralized water to the volume. The ions were determined by ion chromatography using a DIONEX™ 4000 chromatograph equipped with a DIONEX ION PAC™ cation column (CS3) for the determination of Na, K, Mg and Ca, and

for the determination of SO_4 a DIONEX ION PAC™ anion column (AS4) was used.

EXAMPLE 1

1000 g of washed and dried lemon peel, ground to a particle
5 size less than 1 mm was added to a solution of 55.6 ml
concentrated sulphuric acid (95%) in 3500 ml of demineral-
ized water. After stirring briefly the mixture was left to
stand for 22 hours at 22°C whereafter 168 g of NaHCO_3 was
added and the resulting mixture was kneaded until it became
10 homogeneous and the pH had reached a stable level of 4.2.

The paste-like mixture was spread in a thin layer on trays
and dried for 16 hours at 50°C in a drying cupboard to
obtain 1125 g of a product which was ground in a laboratory
mill to a particle size of at the most 0.5 mm. The degree
15 of esterification of the pectic substances was determined
and was found to be 62.7%.

EXAMPLE 2

1000 g of dried lemon peel having a content of galacturonic
acid of 38.1% and a particle size less than 0.5 mm was
20 mixed with 3500 ml of demineralized water containing 55.6
ml concentrated sulphuric acid (96%). The resulting mixture
was left for 22 hours at 20°C after which the mineral acid
was neutralized by adding 168 g of NaHCO_3 followed by
kneading the mixture for 0.5 hour. Drying on trays in a
25 drying cupboard at 50-60°C gave 1112 g of a product with a
dry matter content of 95.2% by weight.

The product was ground in a laboratory mill to a particle
size of 0.5 mm or less. By analysis the degree of esterifi-
cation was found to be 61.0%, the content of galacturonic

acid to be 32.7% and the pH of a 1% aqueous suspension was 3.7. The content of AAIS was 82.2% by weight.

From a 100 g sample of the product the soluble pectin was extracted as described under materials and methods. The content hereof was found to be 26.9% by weight. The water-soluble pectin had a η_{red} of 0.434, a degree of esterification of 62.7% and a galacturonic acid content of 66.0% by weight.

The proportion of the total pectic substances in the product which had been converted to water-soluble pectin was calculated in the following way:

- (1) Content of galacturonic acid in product
= $1112 \times 0.327 = 363.6 \text{ g}$
- (2) Content of galacturonic acid in water-soluble pectin
= $1112 \times 0.269 \times 0.66 = 197.0 \text{ g}$
- (3) Proportion of water-soluble pectin
= $197.0/363.6 = 54.3\%$

EXAMPLE 3

257 g of 4N sulphuric acid was added to 2060 g of tap water. This solution was heated to 75°C followed by the addition under stirring hereto of 1000 g of dried and ground lime peel with a particle size of at the most 0.5 mm. This raw material had a content of galacturonic acid of 39.3%. The resulting mixture was kneaded for 1 hour at 75°C and then cooled to room temperature. 47 g of CaCO_3 was added and the kneading continued for an other hour until the added acid had been neutralized.

After drying of the paste-like mixture at 50-60°C for 20 hours 1080 g of a product with a dry matter content of 92.3% was obtained. Grinding of the product in a laboratory

mill gave a free-flowing powder with a particle size of at the most 0.5 mm.

By analysis of the product the following values were found:

| | | |
|---|-------------------------------|-------|
| | Degree of esterification | 61.9% |
| 5 | Galacturonic acid | 34.5% |
| | pH in a 1% aqueous suspension | 3.61 |
| | AAIS | 80.6% |

The product had a content of water-soluble pectin of 26.9% by weight. This content of water-soluble pectin had the
10 following characteristics: a η_{red} of 0.346, a degree of esterification of 65.0% and a content of galacturonic acid of 64.4%.

When calculated in the same manner as in Example 2 the
15 proportion of pectic substances which was converted into water-soluble pectin was found to be 50.2%.

EXAMPLE 4

1000 g of dried and ground lime peel was processed as described in Example 3 with the exception that the holding
20 temperature was 71-74°C. There was obtained 1070 g of a product with a dry matter content of 91.9% by weight. This product had the following characteristics:

| | | |
|----|-------------------------------|-------|
| | Degree of esterification | 63.4% |
| | Galacturonic acid | 33.6% |
| | pH in a 1% aqueous suspension | 3.6 |
| 25 | AAIS | 81.5% |

After extraction of the water-soluble pectin the content hereof in the product was found to be 30.9%. The water-soluble pectin had the following characteristics: the η_{red}

was 0.358, the degree of esterification was 65.3% and the content of galacturonic acid was 67.4%.

The proportion of water-soluble pectin in the product relative to the total content of pectic substances was
5 62.0%.

EXAMPLE 5

1000 g of dried and ground lime peel was processed essentially as described in Example 4. 2200 g of water was used, and the treatment time was 1.5 hours. 1080 g of product was
10 obtained wherein the dry matter content was 92.2%. By analysis of the product the following values were found:

| | | |
|----|-------------------------------|-------|
| | Degree of esterification | 63.7% |
| | Galacturonic acid | 33.8% |
| | pH in a 1% aqueous suspension | 3.6 |
| 15 | AAIS | 85.6% |

The product contained 30.2% by weight of water-soluble pectin with the following characteristics: a η_{red} of 0.354, a degree of esterification of 68.9% and a galacturonic acid content of 61.8%.

20 The proportion of water-soluble pectin in the product relative to the total content of pectic substances was 55.2%.

EXAMPLE 6

1000 g of dried and ground lime peel was processed as
25 described in Example 3 with the exception that Na_2CO_3 was used as the neutralizing agent instead of CaCO_3 . The results of extensive analyzes of the resulting product are shown in the below Table 1.

The proportion of water-soluble pectin in the product relative to the total content of pectic substances was 86.0%.

EXAMPLE 7

- 5 The products from Examples 3, 4 and 5 were combined and subjected to a further drying. The combined product was analyzed and the results are summarized in Table 1:

TABLE 1

Chemical Analyses of Products from Example 6 and 7

| 10 | | Example 6 | Example 7 |
|---------------------------|-------------------------------|-----------|-----------|
| | Dry matter | 95.3 % | 94.1 % |
| | Degree of esterification | 61.4 % | 64.4 % |
| | Galacturonic acid | 35.3 % | 34.9 % |
| 15 | Ash | 8.96 % | 8.21 % |
| | Sulphate | 41.3 mg/g | 40.3 mg/g |
| | Na | 19.1 mg/g | 0.64 mg/g |
| | K | 3.31 mg/g | 3.60 mg/g |
| | Mg | 1.05 mg/g | 1.07 mg/g |
| 20 | Ca | 11.1 mg/g | 26.8 mg/g |
| | Fe | 0.15 mg/g | 0.10 mg/g |
| | AAIS* | 69.1 % | 71.4 % |
| | pH in a 1% aqueous suspension | 3.67 | 3.61 |
| Soluble Pectin in Product | | | |
| 25 | Content of soluble pectin | 42.8 % | 32.2 % |
| | Galacturonic acid | 71.2 % | 66.5 % |
| | AAIS* | 84.2 % | 80.7 % |
| | Degree of esterification | 58.6 % | 66.3 % |
| 30 | η_{red} | 0.299 | 0.337 |

AAIS* Acid and alcohol insoluble solids (cellulose, pectin, protein, etc.) which remain after washing with acid 60% isopropanol. This treatment removes soluble carbohydrates, salts and water.

The proportion of water-soluble pectin in the combined product relative to the total content of pectic substances was calculated to be 61.4%.

EXAMPLE 8

5 Water holding capacity

Measurements of the water holding capacity (WHC) of the product from Example 7 were carried out according to the method described by SIK (The Swedish Food Institute) in SIK report no. 3604 by L. Jonsson and R.-M. Jansson, 1989. This method is a modification of the Bauman method (Bauman, G.I.T., 1967, 6, 540). In the presently applied method 0.5 to 1.0 g of test material with a particle size of 0.5 mm or less is soaked in 10 ml demineralized water at room temperature for 30 minutes, followed by centrifugation for 10 minutes at 240 x g using a VARIFUGE 3.2S centrifuge. The water holding capacity was then measured as the amount of water retained by 1 g of material after the specified centrifugation. The results are shown in Table 2:

TABLE 2

20 Water Holding Capacity of Product and Raw Material

| Product | Test Amount g | Retained Water g | WHC g water/g product |
|--------------|------------------|---------------------|--------------------------|
| Example 6 | 0.50 | 4.83 | 9.66 |
| 25 Example 7 | 0.50 | 4.86 | 9.72 |
| Lime peel | 0.50 | 2.51 | 5.02 |

EXAMPLE 9

In-vivo cholesterol-reducing effect

Ten weeks old male Sprague-Dawley rats with a body weight of approximately 175-200 g were housed individually in stainless steel cages and acclimatized on a standard laboratory diet for 1 week before beginning the study. The rats were randomized, based on body weight and placed in groups of eight to be fed either the test diet or a control diet (a cellulose diet). The test diet comprised the product from Example 7. Both diets were formulated to contain 4-5% total dietary fibres and identical amounts of proteins, fat, starch, sugars, vitamins, minerals, cholic acids and cholesterol. The rats were weighed at the start of the feeding of diets. Food and water were offered ad libitum for 3 weeks. The final body weights of the rats were measured at the end of this 3 week period, the rats were anesthetized, and blood samples were obtained by cardiac puncture. The livers were removed and frozen together with the plasma samples. The samples were kept at -20°C until they were analyzed.

Serum cholesterol measurements were based on the determination of hydrogen peroxide generated by the catalytic oxidation of cholesterol using the Abbott VP Analyzer. Serum triglycerides were determined by measuring the decrease of the absorbance occurring when NADH is oxidized to NAD, also using the Abbott VP Analyzer. Liver cholesterol was measured as described by Chen & Anderson, 1979, J. Nutr., 109, 1028-1034. The results of the study are summarized in Table 3:

TABLE 3

Cholesterol-reducing Effect in Rats

| | Control (cellulose diet) | Test (product/Example 7) |
|-----------------------------|-----------------------------|-----------------------------|
| 5 | | |
| Body weight, initial (g) | 246 | 239 |
| Body weight, final (g) | 341 | 323* |
| Serum cholesterol (mg/dl) | 169 | 116* |
| Serum triglycerides (mg/dl) | 229 | 175 |
| 10 Liver cholesterol (mg/g) | 37.1 | 27.2* |

* Significantly different from cellulose ($p < 0.05$)

EXAMPLE 10

The gelling properties of the product

- 15 The gelling properties of the products obtained in Examples 6 and 7 were determined according to the IFT SAG method (Food Technology, 1959, vol. XIII, no. 9, 496-500). The gel strengths of the two samples of product were:

| | | |
|----|------------------------|---------|
| | Product from Example 6 | SAG° 56 |
| 20 | Product from Example 7 | SAG° 48 |

EXAMPLE 11

The viscosity of the product

The viscosities of the products from Examples 6 and 7 were determined in the following way:

- 25 Twenty-five g of product was moistened with 25 ml methanol. 500 g of boiling water was added during agitation. The

solution was cooled to 25°C and adjusted for evaporated water to 500 g. The viscosity was measured by a Brookfield LVT viscometer using spindle no. 3, 60 rpm. The viscosities of the 5% solution (w/w) for the two products in question were:

| | |
|------------------------|------------|
| Product from Example 6 | 512 mPa·s |
| Product from Example 7 | 622 mPa·s. |

EXAMPLE 12

257 g of 4N sulphuric acid was added to 2060 g of tap water. This solution was heated to 75°C, followed by the addition under stirring of 1000 g of dried and ground orange peel having a particle size of at the most 0.5 mm and a galacturonic acid content of 33.6% by weight. The resulting mixture was kneaded for 1 1/4 hours at 75°C and then cooled to room temperature. 47 g of CaCO₃ was added and the kneading continued for 1 hour until the added acid had been neutralized.

After drying of the paste-like mixture at 50-60°C for 20 hours, 1065 g of a crude pectin-containing product having a dry matter content of 94.2% by weight was obtained. Grinding of the product in a laboratory mill resulted in a free-flowing powder with a particle size of at the most 0.5 mm.

By analysis of the resulting powder, the following values were found:

| | | |
|----|-------------------------------|-------|
| 25 | Degree of esterification | 61.0% |
| | Galacturonic acid | 31.6% |
| | pH in a 1% aqueous suspension | 4.61 |
| | AAIS | 72.8% |
| | Ashes | 9.81% |
| 30 | Sulphate | 4.2% |
| | Ca | 3.39% |
| | Mg | 0.12% |
| | Na | 0.14% |
| 35 | K | 0.46% |

The water holding capacity of the product was 4.26 g water/g of product.

The product had a content of water-soluble pectin of 13.8% by weight. This content of water-soluble pectin had the following characteristics: a η_{red} of 0.335, a degree of esterification of 66.1% and a content of galacturonic acid of 57.9%.

When calculated in the same manner as in Example 2 the proportion of pectic substances which had been converted into water-soluble pectin was found to be 25.3%.

EXAMPLE 13

1000 g of dried and ground orange peel with a galacturonic acid content of 33.6% by weight was processed as described in Example 12.

1070 g of a crude pectin-containing product was obtained in which the dry matter content was 94.0% by weight. This product had the following characteristics: degree of esterification: 61.0%, content of galacturonic acid: 31.7%, pH in a 1% aqueous suspension: 4.61, AAIS: 75.5%.

Analysis of the content of ashes of the product and the composition hereof gave the following results:

| | | |
|----|----------|-------|
| | Ashes | 9.68% |
| | Sulphate | 4.6% |
| | Ca | 3.39% |
| 25 | Mg | 0.12% |
| | Na | 0.15% |
| | K | 0.46% |

The water holding capacity of the product was 4.70 g water/g product.

After extraction of the water-soluble pectin, the content hereof in the product was found to be 15.4% by weight. The characteristics of the water-soluble pectin of the product were the following:

5

| | |
|-------------------------------------|-------|
| Degree of esterification: | 70.0% |
| Galacturonic acid: | 56.8% |
| Reduced viscosity (η_{red}): | 0.350 |

The proportion of water-soluble pectin in the product relative to the total content of pectic substances was 27.6%.

10

EXAMPLE 14

1000 g of sugar beet fibers having a galacturonic acid content of 31.5% by weight was processed essentially as described in Example 12 with the exception that the reaction time was 1 1/2 hours instead of 1 1/4 hours. 1139 g of a crude pectin-containing product was obtained wherein the dry matter content was 93.5% by weight.

15

By analysis of the resulting product, the following values were found:

20

| | |
|-------------------------------|--------|
| Degree of esterification | 67.4% |
| Galacturonic acid | 28.8% |
| pH in a 1% aqueous suspension | 4.11 |
| AAIS | 63.3%. |

Analysis of the content of ashes of the product and the composition hereof gave the following results:

25

| | |
|----------|-------|
| Ashes | 9.29% |
| Sulphate | 4.1% |
| Ca | 2.24% |
| Mg | 0.18% |
| Na | 0.13% |
| K | 0.38% |

30

The water holding capacity of the product was 3.78 g water/g product.

The product contained 20.5% by weight of water-soluble pectin having the following characteristics:

| | | |
|---|------------------------------------|--------|
| 5 | Degree of esterification | 56.8% |
| | Galacturonic acid | 57.4% |
| | Reduced viscosity (η_{red}) | 0.105. |

The proportion of water-soluble pectin in the product relative to the total content of pectic substances was
10 40.9%.

EXAMPLE 15

1000 g of dried and ground orange peel having a dry matter content of 93.2% by weight and a galacturonic acid content of 33.6% was suspended in a solution of 60.4 g of 98% (w/v)
15 sulphuric acid in 2340 g of demineralized water. The resulting mixture was stirred and kneaded for 1 hour and 25 minutes at 75°C followed by cooling of the mixture to room temperature. 64.7 g of anhydrous sodium carbonate was added and the stirring/kneading was continued until the added
20 sulphuric acid had been neutralized.

The resulting paste-like neutralized mixture was dried in a drying cupboard at 50-60°C until the following day and subsequently subjected to a grinding process which gave
1091 g of a free-flowing powder of a crude pectin-containing product having the following characteristics:
25

| | | |
|---|-------------------------------|-------|
| | Degree of esterification | 55.8% |
| | Galacturonic acid | 28.6% |
| | pH in a 1% aqueous suspension | 3.95 |
| | AAIS | 76.2% |
| 5 | Na | 2.3% |
| | K | 0.5% |
| | Ca | 1.7% |
| | Mg | 0.1% |
| | Sulphate | 5.7% |

10 The product had a content of water-soluble pectin of 24.0% by weight. This content of water-soluble pectin had the following characteristics: a η_{red} of 0.340, a degree of esterification of 63.7% and a content of galacturonic acid of 59.3%.

15 The proportion of water-soluble pectin in the product relative to the total content of pectic substances was 49.8%.

Additionally, the viscosity of the resulting pectin product was measured by means of a Haake Viscotester according to the method described above. These viscosity measurements the results of which are also indicative of the solubility of the pectin product were carried out with the pectin product as such and with the same amount of pectin product in the presence of varying amounts of the following phosphates (P): sodium hexametaphosphate (A), disodium phosphate (B) and tetrasodium pyrophosphate (C). The amounts of the phosphates were as follows (% by weight relative to the amount of pectin product): 2, 5, 10, 15, 25, 50 and 100. The results are summarized in the below table:

TABLE 4

The effect of phosphates on the viscosity
of the crude pectin product

| | P | A | | B | | C | |
|----|-----|------|-----|------|-----|------|-----|
| | % | mPas | pH | mPas | pH | mPas | pH |
| 5 | 0 | 8 | | 8 | | 8 | |
| | 2 | 11 | | | | 9 | |
| | 5 | 23 | | | | 51 | 5.7 |
| 10 | 10 | 51 | 4.3 | 17 | | 17 | |
| | 15 | 46 | | 58 | | 7 | |
| | 25 | 29 | | 26 | | 5 | 8.2 |
| | 50 | 28 | 5.5 | 7 | 7.7 | 4 | |
| | 100 | 27 | | 5 | 7.9 | 4 | |

15

From the above results it appears that the tested pectin product is only partially soluble in water when a phosphate is not present. However, in the presence of a phosphate the viscosity increases which may be interpreted as a higher degree of solubility of the pectin product. It is concluded that the optimum viscosity is observed when the following amounts (as defined above) of the phosphates are present: sodium hexametaphosphate (A): 10%, disodium phosphate (B): 15% and tetrasodium pyrophosphate (C): 5%. During the viscosity measurements it was furthermore observed that an optimum viscosity was observed at a temperature of the reaction mixture in the range of 20-25°C.

The gelling properties of the product obtained in the present Example were determined according to the IFT SAG method (Food Technology, 1959, vol. XIII, no. 9, 496-500) without and in the presence of 10% by weight of sodium hexametaphosphate relative to the amount of pectin product. The gel strengths of the two samples of product were:

30

Product without phosphate SAG° 29
Product with phosphate SAG° 53

These results indicate that pectin is released at boiling conditions from the product in amounts which are sufficient
5 to obtain a gel even without the addition of phosphates.

EXAMPLE 16

Preparation of hamburger buns containing crude pectin product

Batches of buns were prepared based on the following base
10 recipe:

| | | |
|----|---------------------|-----------------|
| | Wheat flour | 3000 g |
| | Salt | 54 g |
| | Sugar | 120 g |
| | Dextrose | 30 g |
| 15 | Compressed yeast | 150 g |
| | Fat (m.p. 35°C) | 60 g |
| | DIMODAN PM™ Hydrate | 60 g |
| | PANODAN™ 80 | 15 g |
| | Ascorbic acid | 400 ppm |
| 20 | GRINDAMYL™ A 1000 | 120 ppm |
| | L-cystein | 20 ppm/kg flour |
| | Water | 1800 g |

(DIMODAN PM™ Hydrate is a monoglyceride additive based on tallow or lard (Grindsted Products); PANODAN™ 80 is an
25 emulsifying additive comprising diacetyl tartaric acid ester of monoglycerides and diglycerides and 20% by weight CaCO₃ as an anticaking agent (Grindsted Products); GRIN-DAMYL™ A 1000 is an Aspergillus oryzae α-amylase product).

Four batches of buns were prepared according to the follow-
30 ing recipes:

1. The base recipe
2. 1 + 1% SOBALG™ FD 155 + 2% water
3. 1 + 2% crude pectin product from Example 15 with 0.3% sodium hexametaphosphate + 2% water
- 5 4. 1 + 4% crude pectin product from Example 15 with 0.6% sodium hexametaphosphate + 3% water.

(SOBALG™ FD 155 is a sodium alginate product (100%) from Grindsted Products.)

- 1800 g batches of buns were prepared by mixing the ingredients in a Tweedy™ mixing apparatus without vacuum for about 1 minute. The resulting dough, the temperature of which reached about 28°C rested for 5 minutes at room temperature prior to moulding using a Fortuna™ moulder followed by proofing the moulded bun dough for 60 minutes at 40°C and
- 15 85% RH and baking at 220°C for 10 minutes.

The baked buns were tested according to standard procedures for (1) volume (cm³/g) and for (2) consistency after freezing at -20°C for 24 hours and thawing in a microwave oven for about 30 seconds at 500 W.

- 20 The volume values were as follows: recipe no. 1 (control): 7.5; recipe no. 2 (control with added alginate): 5.9; recipe no 3: 7.0; recipe no. 4: 6.9. These results indicate that the addition of the crude pectin product ingredient resulted in essentially the same volume as that of the
- 25 control product without alginate.

- In the evaluation of the consistency of bun batches a sensory panel assessed the toughness of the frozen and thawed buns. The test batches comprising the pectin product (recipe nos. 3 and 4) had a higher score than both control
- 30 batches. These results indicate that the crude pectin

product according to the invention when added to a dough mixture can counteract the well-known development of toughness in baked bread after freezing and thawing.

EXAMPLE 17

5 Preparation of strawberry jam using the crude pectin product as the gelling agent

A batch of strawberry jam was prepared according to the following recipe:

| | | |
|----|-----------------------------------|---------|
| | Crude pectin product (Example 15) | 0.60% |
| 10 | Water | 7.20% |
| | Strawberry puree | 45.00% |
| | Sugar | 59.33% |
| | Na-hexametaphosphate | 0.12% |
| | Citric acid, 50% (w/v) | 0.90% |
| 15 | Total | 113.15% |
| | Evaporation during process | 13.15% |
| | Yield | 100.00% |

The pectin product and the hexametaphosphate were added to about 80°C hot water in a high speed mixer. The strawberryes and sugar were mixed and brought to the boil. The pectin product solution was added to the fruit/sugar mixture and boiling was continued until a level of soluble solids (SS) of 65% was reached and finally, the citric acid was added. The resulting jam had a pH of 3.1.

- 25 The gelling of the jam was characterized by measuring the internal strength of the gel by means of a Volland Stevens Texture Analyser as described by Ikkala (Proceedings of the Third International Conference and Industrial Exhibition, North East Wales Institute, Wrexham, U.K., 1985, 3-15).
- 30 Using a plunger velocity of 0.5 mm/second and a penetration of 10 mm an internal strength value of 47 g was measured.

This confirms that the crude pectin product is useful as a gelling agent in fruit jams, in particular in the presence of a phosphate. By varying the amounts of the crude pectin product and the phosphate it is possible to obtain a desired gelling of fruit jams.

EXAMPLE 18

Preparation of pectin jellies using the crude pectin product as a gelling agent

In the manufacturing of the confectionery product, pectin jellies the desired gel strength is obtained by the incorporation of highly purified pectin products. Experiments were carried out to study the usefulness of the present crude pectin product as a gelling agent in pectin jellies. The following recipe was selected:

| | | |
|----|-----------------------------------|---------|
| 15 | Crude pectin product (Example 15) | 4.00% |
| | Water | 50.00% |
| | Sugar | 50.65% |
| | Glucose syrup, 42 DE, 45% SS | 30.00% |
| | Na-hexametaphosphate | 0.60% |
| 20 | Citric acid, 50% (w/v) | 0.50% |
| | Total | 135.75% |
| | Evaporation | 35.75% |
| | Yield | 100.00% |

25 Citric acid was dissolved in water at 70°C. The pectin product and the phosphate were added to this solution under vigorous agitation. The sugar and syrup ingredients were heated to boiling and the pectin product-containing solution was added hereto and boiling continued until a level of soluble solids of 78% had been reached by evaporation. Finally the resulting mixture was transferred to moulds and left for setting for about 24 hours.

The resulting pectin jellies had an acceptable texture and reasonable gel strength indicating that the crude pectin product may be a useful gelling agent in gelled confectionery products such as pectin jellies.

5 EXAMPLE 19

Fruit juice containing the crude pectin product

Purified pectin products are frequently used as ingredients in fruit juices in order to provide a desired viscosity in the juice resulting in a mouthfeel of "richness". Experiments were carried out to evaluate whether the crude pectin product can replace purified pectins as the viscosity increasing agent in fruit juices. As an example a batch of orange juice was prepared according to the following recipe:

| | | |
|----|----------------------------------|--------|
| 15 | Crude pectin product (Example 5) | 0.50% |
| | Sugar | 4.65% |
| | Na-hexametaphosphate | 0.05% |
| | Water | 79.80% |
| | Orange juice concentrate | 15.00% |

20 The resulting ready-to-use orange juice had a mouthfeel which was comparable to that of an orange juice containing a purified pectin product (MEXPECTIN[®] RS 461, Grindsted Products) as the viscosity increasing agent.

CLAIMS

1. A crude pectin product containing plant tissue material with microscopically recognizable plant tissue structures, the product having a dry matter content of at least 85%,
5 wherein the dry matter content comprises:

1) 5-45% by weight of pectic substances calculated as galacturonic acid and having a degree of esterification in the range of 45-90%, the proportion of the pectic substances which is water-soluble being in the range of 10-80% by
10 weight, which water-soluble pectic substances have a galacturonic acid content of at least 50% and a content of acid and alcohol insoluble solids (AAIS) in the range of 60-90% by weight as defined as solids remaining after washing with acidic 60% (v/v) isopropanol, and a reduced viscosity (η_{red}) which is at
15 least 0.050 L/g as determined by measuring the specific viscosity (η_{sp}) of a solution of the water-soluble pectic substances at 20°C in a Hoeppler falling ball viscometer using a buffer solution consisting of 1%
20 (w/w) sodium hexametaphosphate in distilled water in which the pH is adjusted to 4.5, and calculating the reduced viscosity,

2) 5-15% by weight of ashes comprising a proportion of alkaline and/or alkaline earth metals in the range of 30-
25 50% by weight, and

3) 40-90% by weight of non-pectic plant tissue materials comprising cellulose, hemicellulose, organic acids and water-soluble carbohydrates,

said product having a content of acid and alcohol insoluble
30 solids (AAIS) in the range of 50-80% by weight as defined as solids remaining after washing with acidic 60% (v/v) isopropanol, the product being further characterized in that

a) the pH of an aqueous 1% suspension thereof is in the range of 3-5,

b) the water holding capacity as determined by soaking 0.5 to 1 g thereof having a particle size of at the most 0.5 mm
5 in 10 ml demineralized water at ambient temperature for 30 minutes, centrifuging the soaking mixture for 10 minutes at 240 x g and measuring the amount of water retained per g of product, is at least 4 g water/g,

2. A product according to claim 1, wherein the proportion
10 of pectic substances in the dry matter is at least 25% by weight.

3. A product according to claim 1 or 2 in which the plant tissue material dry matter contains at least 10% by weight, preferably at least 15% by weight, of pectic substances.

15 4. A product according to claim 3, wherein the plant tissue material is selected from the group consisting of peel, pulp or rag from citrus fruits, apple pomace, pear pomace, potato peel, sugar beet pulp, skin of grapes, pea pods, carrot fibres, fresh fruits, vegetables and mixtures there-
20 of.

5. A product according to claim 1, wherein the dry matter content is at least 90% by weight, and in particular at least 95% by weight.

25 6. A product according to claim 1, wherein the degree of esterification of pectic substances is at least 50%, and preferably 60%.

7. A product according to claim 1, wherein the proportion of pectic substances which is water-soluble is at least 40% by weight.
8. A product according to claim 7, wherein the proportion of pectin substances which is water-soluble is at least 50% by weight.
9. A product according to claim 1, wherein the water-soluble pectic substances have a galacturonic acid content of at least 70% by weight.
- 10 10. A product according to claim 1, wherein the water-soluble pectic substances have a content of acid and alcohol insoluble solids (AAIS) of at least 75% by weight.
11. A product according to claim 1, wherein the dry matter comprises at least 8% by weight of ashes.
- 15 12. A product according to claim 1, wherein the dry matter comprises an inorganic or an organic acid residue in an amount not naturally occurring in the selected plant cell material.
13. A product according to claim 12, wherein the inorganic acid residues are selected from the group consisting of chlorides, sulphates, phosphates and nitrates.
14. A product according to claim 12, wherein the organic acid residue is selected from the group consisting of formates, lactates, citrates, maleates and oxalates.
- 25 15. A product according to claim 1, wherein the alkaline and/or alkaline earth metals comprises a proportion of calcium of at least 25% by weight, preferably at least 50% by weight, and in particular 70% by weight.

16. A product according to claim 1, wherein the pH of an aqueous 1% suspension is in the range of 3.5 to 4.5.
17. A product according to claim 1, wherein the water-soluble pectic substances have a reduced viscosity of at least 0.150, preferably at least 0.300, and in particular at least 0.500 L/g.
18. A product according to claim 1, wherein the water holding capacity is at least 6 g water/g and preferably at least 9 g water/g.
19. A product according to any of claims 1-18, wherein the feeding of rats with cholesterol reducing amounts thereof for at least a period of 3 weeks results in a reduction of the amount of serum and liver cholesterol of at least 25% relative to amounts of serum and liver cholesterol of animals fed a control diet not containing the product.
20. A product according to any of claims 1-19 which is in the form of a substantially free-flowing powder consisting essentially of particles of a size of at the most 1.0 mm.
21. A method for producing a crude pectin product, comprising subjecting plant tissue material containing pectic substances and having microscopically recognizable plant tissue structures to conditions which will convert at least part of the water-insoluble pectic substances thereof to water-soluble pectic substances in which substances the degree of esterification initially present in the water-insoluble pectic substances is substantially preserved, followed by drying the resulting material to a water content of 15% by weight or less and optionally comminuting the dried material, without at any stage adding water in an amount which will result in a water content substantially higher than the original water content of the plant tissue material in its fresh state, said original water content being at the most 90% of the plant material fresh

weight, the drying of the material being performed without any substantial concomitant removal of dry matter, such as by evaporation of water.

22. A method according to claim 21, wherein the plant
5 tissue material in its dry matter contains at least 5% by weight, preferably at least 10% by weight, and in particular at least 15% by weight of pectic substances.

23. A method according to claim 21 or 22, wherein the plant
10 tissue material is selected from the group consisting of peel, pulp or rag from citrus fruits, apple pomace, pear pomace, potato peel, sugar beet pulp, skin of grapes, pea pods, carrot fibres, fresh fruits, vegetables and mixtures thereof.

24. A method according to any of claims 21-23, wherein
15 essentially all the pectic substances present in the plant tissue material are insoluble.

25. A method according to claim 21, wherein the degree of esterification of the pectic substances is in the range of 45-90% and preferably at least 60%.

20 26. A method according to claim 21, wherein the fresh plant tissue material is first subjected to a washing with cold water to remove at least part of the water-soluble substances present in the fresh material and/or a comminution process to obtain a particle size of at the most 10 mm.

25 27. A method according to claim 26, wherein the washed and/or comminuted plant tissue material is dried.

28. A method according to any of claims 21-27, wherein the
conditions which will convert at least part of the water-insoluble pectin substances to water-soluble pectic sub-
30 stances are established by adding an inorganic or organic acid to the plant tissue material in an amount sufficient

- to reduce the pH to a value in the range of 0-5, preferably in the range of 1-3, keeping the resulting mixture at a temperature and for a period of time sufficient to obtain conversion of the desired proportion of non-soluble pectic substances to water-soluble substances, said desired proportion being in the range of 25-80% by weight, followed by adjusting the pH to a higher value within the range of 2.5-8, preferably in the range of 3-5 by the addition of the necessary base equivalent.
29. A method according claim 28, wherein the inorganic acid is selected from hydrochloric acid, phosphoric acid, sulphuric acid and nitric acid.
30. A method according to claim 28, wherein the organic acid is selected from formic acid, lactic acid, citric acid, oxalic acid and malic acid.
31. A method according to claim 30, wherein the organic acid is provided by the addition of a microorganism capable of converting plant tissue material components to organic acids such as lactic acid bacteria.
32. A method according to claim 28, wherein the mixture is kept at a temperature ranging from ambient temperature to about 100°C, preferably in the range of 50-80°C.
33. A method according to claims any of claims 28-32, wherein the mixture having a pH in the range of 0-5 is left to stand for from 1 hour to 24 hours
34. A method according to claim 28, wherein pH is adjusted to a higher value by the addition of a base selected from the group consisting of NaOH, KOH, K_2CO_3 , NH_4OH , $CaCO_3$, Na_2CO_3 , $NaHCO_3$, CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$, $MgCO_3$ and $Al(OH)_3$.

35. A method according to claim 21, wherein the conditions which will convert at least part of the water-insoluble pectin substances to water-soluble pectic substances are established by adding an enzyme to the plant tissue material.

36. A method according to claim 21, wherein the conditions which will convert at least part of the water-insoluble pectic substances to water-soluble pectic substances are established by adding an enzyme-producing microorganism to the plant tissue material.

37. A method according to claim 21, wherein the plant tissue material in which at least part of the water-insoluble pectic substances have been converted is dried at a temperature ranging from ambient temperature to about 150°C.


38. A method according to claim 37, wherein the drying is carried out in a drying equipment selected from a drying oven, a fluid bed dryer, a band dryer and a drum dryer.

39. A method according to claim 37 or 38, wherein the drying is carried out at air pressures below atmospheric pressures.

40. Use of the product as defined in claims 1-20 as a water absorbing and/or water holding material.

41. Use of the product as defined in claims 1-20 as a thickening and/or gelling agent.

42. Use of the product as defined in claims 1-20 as a dietary fibre additive.

| | | |
|--|---|--|
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| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| IPC ⁵ : C 08 B 37/06, A 23 L 1/308, A 61 K 31/725, A 61 L 15/28 | | |
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| III. DOCUMENTS CONSIDERED TO BE RELEVANT * | | |
| Category * | Citation of Document, ** with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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DK 9100072
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| GB-A- 472974 | | None | |
| FR-A- 1584509 | 26-12-69 | None | |

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